vibration to the 1300 cm.$^{-1}$ region appears to hold more merit.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Infrared Study of the Acetone–Water System

BY PETER J. LUCCHESI[1]

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The infrared spectrum of liquid acetone gives a sharp absorption band at 3400 cm.$^{-1}$ and a broader band at 3600 cm.$^{-1}$. The latter increases in intensity upon addition of small quantities of water to the sample and is attributed to traces of water. Beer's law is not obeyed. The band does not disappear completely after repeated drying of acetone. The 3600 cm.$^{-1}$ band decreases in intensity when crystalline powders are mixed with the acetone-water solutions. This band can be considered a result of intermolecular hydrogen bonding, whereas the 3400 cm.$^{-1}$ band is probably the overtone of the carbonyl band which occurs at 1740 cm.$^{-1}$.

Introduction

It was the purpose of this investigation to study the changes in the infrared absorption spectrum of liquid acetone caused by the presence of small amounts of water, and to determine whether such effects could be useful in gaining insight into the interaction between water and carbonyl compounds at low water concentrations.

Bawn,[2] Lecomte,[3] and Marton[3] have reported an absorption band for liquid acetone which occurs in the infrared region of 2.90 μ. Water vapor also absorbs in this region, the absorption having been assigned to the overlapping of the ν_3 and ν_1 fundamentals. This band, as expected, is shifted to lower wave numbers in the condensed phase so that the net effect observed is that the spectrum of liquid acetone containing small amounts of water gives a sharp absorption band at 3400 cm.$^{-1}$ and a broader band in the 3600 cm.$^{-1}$ region. The band at 3400 cm.$^{-1}$ is not significantly altered by the addition of small amounts of water to the sample, whereas the absorption at 3600 cm.$^{-1}$ increases with increasing concentration of water in acetone. This increase is obvious from Fig. 1, which was reproduced from the spectra recorded by the spectrophotometer. The ν_2 fundamental of water, which occurs at 1595 cm.$^{-1}$,[4] is masked in acetone solutions by the strong absorption of the solvent in this region. The absorption in the 3400 cm.$^{-1}$ region has been observed at slightly higher wave numbers in the gas phase, and is known to occur in the liquid phase for some ketones, aldehydes and alcohols.[5] The effect of adding traces of water to acetone gives some insight regarding the nature of 3400 and 3600 cm.$^{-1}$ bands observed. Although intermolecular hydrogen bonds give absorption in the former region,[6] the low concentration of the enol form to be expected for acetone, and the fact that the 3400 cm.$^{-1}$ band is little changed by the addition of water, show that this band is not due to such bonds. A likely possibility is that the band represents the first overtone of the carbonyl band, which occurs near 1740 cm.$^{-1}$. The band at 3600 cm.$^{-1}$, however, is strongly affected by traces of water and the absorption in this region is most likely due to intermolecular hydrogen bonding between acetone and water. The strength of this interaction is evidenced by the extreme difficulty observed in attempts to eliminate the 3600 cm.$^{-1}$ absorption by repeated drying of the acetone.

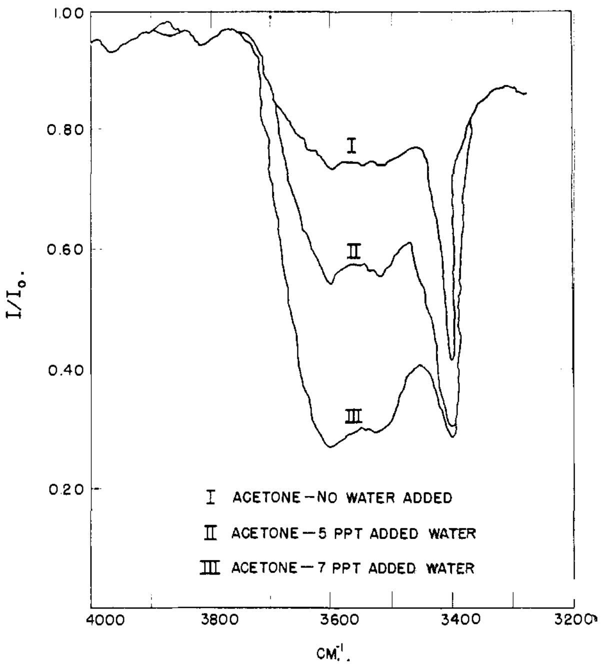

Fig. 1.—Spectrum of acetone-water mixtures in the 3600 cm.$^{-1}$ region. Curve I represents purified acetone; curves II and III show the effect of adding 5 and 7 p.p.t. by volume of water to the sample.

Experimental

The acetone used as starting material was obtained from the Eastman Kodak Company. The purification of this acetone was accomplished using the method of Shipsey and

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[1] Esso Research and Engineering Co., Linden, New Jersey.

[2] C. E. H. Bawn, *J. Chem. Soc.*, **135**, 1189 (1932).

[3] J. Lecomte, *Compt. rend.*, **180**, 1481 (1925); L. Marton, *Z. physik. Chem.*, **117**, 97 (1925).

[4] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 487.

[5] American Petroleum Institute Research Project 44, "Infrared Spectral Data," 1953.

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954.

Werner[7] in which a crystalline product, containing three moles of acetone per mole of sodium iodide, is prepared. Distillation of this compound and repeated distillation of the product was followed by drying over calcium chloride in a moisture-free dry box. All sampling operations and preparation of solutions were carried out in the dry box which was flushed with nitrogen during the operation. Alternatively, the commercial acetone was repeatedly fractionated and the fraction boiling at 56.1° collected. The products prepared by both methods gave the same boiling point and refractive index, *i.e.*, n^{20}_D 1.3590. The reported refractive index is 1.3591.[8] The acetone purified by these procedures did not decolorize dilute permanganate solutions. It was found necessary to transfer the solution into the sample cell in a dry box because, in some cases, filling the cells in the laboratory air introduced traces of water. The sample cells were fixed thickness sodium chloride cells (0.2 mm.) which were not affected by acetone containing small amounts of water. All measurements were carried out with cells of the same thickness and the spectra were measured on the Perkin-Elmer Model 21 recording spectrophotometer, with sodium chloride optics. Wave length calibrations were made using the known absorption bands of water vapor and carbon dioxide.

Results

Figure 1, curve I, gives the absorption spectrum of an acetone sample partially purified as described above. The presence of water in the sample is indicated by the absorption in the 3600 cm.$^{-1}$ region. Known volumes of distilled water were added to this sample by means of calibrated micropipets and the increased absorption in this region is illustrated by curves II and III, which were taken with samples to which increasing amounts of water had been added. The Beers' law plot was obtained from the absorbance at 3600 cm.$^{-1}$ plotted against the concentration of water added, in parts per thousand by volume, to purified acetone. The highest per cent. transmittance obtained in the case of the purest acetone prepared was of the order of 90%. In the range 0–20 p.p.t. of water added to this sample the curve is not linear but shows positive deviations from linearity and levels off at higher water concentrations (13–20 p.p.t. added water). Extrapolation of the smooth curve to zero absorbance gave an estimate of the amount of water present in the purified sample, assuming the 3600 cm.$^{-1}$ absorption of the purified sample was due to traces of water. This procedure gave approximately 2.5 p.p.t. by volume, or about 0.2% by weight. In the initial portion of the curve, to approximately 10 p.p.t. of added water, the curve gave satisfactory results for the estimation of water added to the sample. For five different concentrations in this range the results obtained gave an average deviation from the known amount of water added of 0.08%. However, at higher concentrations the absorbance of the sample is less sensitive to changes in water concentration.

It should be mentioned that a variety of salts (strontium bromide, strontium sulfate and others), when added in excess to an acetone–water solution of known concentration, gave a measurable decrease in the per cent. absorption at 3600 cm.$^{-1}$ but not at 3400 cm.$^{-1}$. This decrease, probably due to adsorption of water on the powder, became greater when the surface area of the solid increased. However, the variations were too small to permit a reliable estimate of apparent surface areas.

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(7) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

(8) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND THE VIRUS LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

A Study of the Kinetics of the Enzymatic Digestion of Deoxyribonucleic Acid[1]

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In a recent paper from this Laboratory dealing with structural models for deoxyribonucleic acid (DNA) with particular emphasis on the two strand model proposed recently by Watson and Crick it was pointed out that a detailed study of the kinetics of the enzymatic digestion of DNA might yield information about different models. For example a one strand structure would be split at each attack by the enzyme. A two strand structure would require at least two attacks and therefore the efficiency of splitting would increase with the square of the number of attacks. A two strand structure with some "preformed gaps," a model proposed in the above mentioned paper, would degrade in a manner intermediate between a single strand model and a continuous two strand model. This communication presents a detailed theory for the degradation of such long chain macromolecules. From the distribution of fragments formed upon random hydrolysis the decrease in the viscosity of such a solution is calculated. The calculation is generalized to include solutions of polymers each molecule of which contains a definite number of chains bound side by side. Certain parts of this treatment are general for molecules polydisperse with respect to both molecular weight and shape. This communication also presents new data on the viscosity and sedimentation changes as a function of the number of enzymatic attacks on the DNA macromolecule. The number of enzymatic attacks is determined in a "*p*H-stat" by measuring the hydrogen ion liberation resulting from the cleavage of the phosphodiester bonds. The theory developed may be applied to the experimental data, and thus the single strand model for the DNA molecule is ruled out. The best agreement is obtained with a doubly stranded model. Moreover the number of preformed gaps in the structure as determined by this study is less than one in about 3000 nucleotides.

Considerable interest has been focussed on the helical model proposed by Watson and Crick[2] for the structure of deoxyribonucleic acid (DNA), and many lines of evidence support the view that DNA, as commonly isolated, is a hydrogen-bonded, intertwined, two strand structure. X-Ray diffraction data and chemical analysis furnish the principal sources of evidence for this model. Furthermore, the hydrodynamic behavior, as revealed by sedi-

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(1) This work was supported by grants from the National Science Foundation, Lederle Laboratories, and The Rockefeller Foundation.

(2) J. D. Watson and F. H. C. Crick, *Nature*, **171**, 737 (1953).